



Metal-loaded ZSM5 zeolites for catalytic purification of dioxin/furans and NO_x containing exhaust gases from MWI plants: Effect of different metal cations

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ABSTRACT

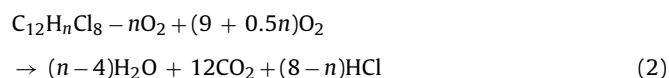
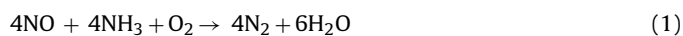
A series of metal loaded ZSM5 including Cu/, Fe/, Mn/ and V/ was prepared and their catalytic activity, selectivity and durability were compared with the commercially used VO_x/TiO₂ catalyst for the combined abatement of NO and *o*-dichlorobenzene (*o*-DCB, model molecule to simulate PCDD/Fs) from the off-gases of a municipal waste incinerator (MWI) plant. Catalysts textural, acid and redox properties have been characterized by N₂ adsorption–desorption isotherms, XRD, NH₃-TPD and H₂-TPR and a higher surface area, acidity and reducibility of the metal loaded zeolite catalysts have been confirmed. By catalytic tests carried out in the experimental conditions close to those employed in MWI plants, it was concluded that VO_x/TiO₂ show higher catalytic performance than metal/zeolite catalysts. A relationship between metal reducibility and the catalyst activity was found. However, zeolites due to their high acidity are less selective to NH₃ oxidation reaction (negligible N₂O formation) and therefore higher NO conversion is obtained in a wider operating temperature window. Using zeolites selectivity to CO is lower, although traces of trichlorobenzene are detected. Both reactions are well fit to first order reaction kinetic over all the catalysts. In addition, neither of the catalysts show evidence of deactivation during 12 h of reaction. Among metal/zeolites, Cu/Z is the most active catalyst, whereas Fe/Z is the less for both NO reduction and *o*-DCB oxidation reactions. Unfortunately, Cu/Z high selectivity to highly chlorinated compounds, like trichlorobenzene, was also found.

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1. Introduction

Metal/zeolite catalysts and especially iron and copper zeolites are being extensively studied in the last years for NO_x abatement by selective catalytic reduction (SCR) with NH₃ in mobile sources. For vehicles it is essential to develop catalysts with high catalytic activity at low temperature as well as wide working window in order to conform efficiently the engine's temperature variations. Otherwise in stationary sources, the catalytic reactor's temperature is usually constant and V₂O₅-WO₃ (MoO₃)-TiO₂ is the commercially used catalyst. In line with the 2000/76/EC Directive of the European Union [1] and in order to cope with increasingly stringent environmental laws, municipal waste incineration (MWI) plants have begun to implement the SCR technology to reduce the NO_x more efficiently than nowadays where NH₃ is added to the combustion

boiler. Some catalyst manufacturers say that SCR catalysts are able to simultaneously destroy dioxin/furans (PCDDs/Fs) and NO_x [2–4] in a unique catalytic process being a highly interesting alternative to the current non destructive method such as fabric filters, scrubbers and activated carbon beds for PCDDs/Fs [2]. To the best of our knowledge, few studies have reported the combined degradation [4,5] and in a previous work [6] we demonstrated the good catalytic performance of VO_x/TiO₂ catalyst in the simultaneous removal of NO (by SCR) and 1,2-dichlorobenzene (*o*-DCB) model molecule of PCDD/Fs (by catalytic total oxidation (CTO)) according to Eqs. (1) and (2), respectively.



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The simultaneous removal NO_x and PCDD/Fs requires even higher temperatures than the independent SCR reaction due to the higher stability of PCDD/Fs [6]. In addition, PCDD/Fs encompass a large amount of chemical compounds with different reactivity so that the catalytic reactor feed and its stability can vary. Therefore, MWI plants are also keen on developing catalysts with a broad operating window.

The NO SCR with NH_3 reaction mechanism is widely studied in the literature and is established that over VO_x/TiO_2 catalyst the reaction starts with the NH_3 adsorption on acid Brønsted site (V-OH) and follows by its activation via redox reaction reducing the adjacent V^{+5} to V^{+4} ($\text{V}=\text{O}$); then, the final step is the reaction between activated NH_3 and gas phase or weakly adsorbed NO, leading to the reoxidation of V^{+4} to V^{+5} [7]. In the case of *o*-DCB oxidation, the first step is also its adsorption on acid sites through its chlorine atom(s) which subsequently can be attacked by mobile oxygen species [8,9]. Therefore, both redox and acid properties seem to be important to obtain a good catalyst for the combined NO and *o*-DCB removal. In this sense many alternative to commercial $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ catalyst have been studied for each reaction, NO reduction [10] and *o*-DCB oxidation [11], separately. In addition to the aforementioned, the use of TiO_2 as a support is limited by the fact that it possesses low resistance to sintering and low surface area. For the other, the high toxicity of vanadium and its high activity oxidizing SO_2 to SO_3 , which could react with H_2O and NH_3 to form NH_4HSO_4 , $(\text{NH}_4)_2\text{S}_2\text{O}_7$ and H_2SO_4 and corrode downstream equipments and deactivate the catalyst. In view of such disadvantages, high surface area and resistance supports as well as non toxic and active metals are needed to look for.

In this work the use zeolite as support due to its high surface area and acidity is proposed. Regarding metal/zeolite catalysts Cu/zeolite is the most studied. It is known that bulk CuO catalyzes the oxidation of NO to NO_2 [12] which react with NH_3 at lower temperature than NO. In addition of that, NO_2 has greater oxidation potential than O_2 so it could assist or at least partially replace O_2 in the PCDD/Fs oxidation [13,14]. Otherwise, Cu^{+2} ions maintain high NO_x conversion at high temperature [12]. Fe exchanged zeolites have received much attention as catalysts for NO SCR reaction due to their good performance at high temperature with low selectivity for NH_3 oxidation reaction [15] and also high activity in N_2O decomposition [16,17]. Therefore, Fe incorporated zeolites are likely to remove together NO_x and PCDD/Fs with high efficiency since they have been also tested for various oxidation applications [18,19]. Finally, in recent years MnO_x based catalysts are widely studied in both reactions independently because it contains various types of labile oxygen, which are necessary to complete the catalytic cycles [10,20,21].

In the light of the above, this work is essentially devoted to determining the catalytic performance of zeolites for the simultaneous removal of NO_x and PCDD/Fs, in simulated conditions close to those employed in MWI plants. For that purpose different metal exchanged zeolites such as Cu/ZSM5, Fe/ZSM5, MnO_x /ZSM5 and VO_x /ZSM5 were compared. VO_x/TiO_2 catalyst is also prepared as a reference.

2. Material and methods

2.1. Catalyst preparation

Catalysts were prepared by different methods, as follows:

VO_x/TiO_2 (V/T) and VO_x /ZSM5 (V/Z) were prepared by wet impregnation. The certain amount of precursor (NH_4VO_3) to obtain 3% of vanadium was dissolved in distilled water and complexed with 2 mols of oxalic acid for 1 mol of vanadium. After maintaining the solution slurry at 35 °C and 0.4 kPa under continuous rota-

tion for 3 h, the solvent was evaporated; the resulting samples were dried overnight at 110 °C and then calcined at 500 °C for 3 h (1 °C/min). As a support, commercial TiO_2 anatase calcined at 520 °C for 3 h from Millennium Inorganic Chemicals—Cristal Global (Cristal ACTiV™ G5) was used. The H-ZSM5 support was prepared by calcining the NH_4 -ZSM5 zeolite supplied by Zeolyst International (Si/Al molar ratio of 25) in air at 550 °C for 3 h.

MnO_x /ZSM5 (Mn/Z) catalyst was also prepared by the wet impregnation. The precursor solution was obtained dissolving the certain quantity of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ to obtain 3% of Mn in distilled water. The impregnation was made slurring the solution at 35 °C and 0.4 kPa under continuous rotation for 3 h. After solvent evaporation, the sample was dried (overnight at 110 °C) and calcined at 520 °C for 3 h.

Cu/ZSM5 (Cu/Z) and Fe/ZSM5 (Fe/Z) were prepared by the so called ion exchange method [12,16]. The ion exchanged samples were prepared dissolving the required amount of $\text{Cu}(\text{COOCH}_3)_2$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in water. The H-ZSM5 support was prepared by calcining the NH_4 -ZSM5 zeolite supplied by Zeolyst International (Si/Al molar ratio of 25) in air at 550 °C for 3 h. Then, 12 g H-ZSM5 were added to 1.5 L of this solution and it was stirred for 24 h at 65 °C. The ion exchanged samples were filtered and washed twice in deionizer water and after that calcined at 500 °C for 3 h. Finally, in order to carry out the catalytic reactions in absence of mass transfer limitations and low pressure drop, all the catalysts were pelletized, crushed and sieved to 0.3–0.5 mm.

2.2. Catalyst characterization

The actual amount of metals in the prepared catalysts were determined by ICP-AES (Horiba Jobin Yvon, Activa) after complete dissolution of the solid samples in 1:3 HNO_3 :HCl mixture followed by few drops of HF at 90 °C.

Textural properties were evaluated by means of N_2 adsorption-desorption isotherms, determined at –196 °C in a Micromeritics TRISTAR II 3020 apparatus in case of TiO_2 support and in a Micromeritics ASAP 2010 equipment in case of zeolitic catalysts. The specific surface areas of the prepared samples were determined by the standard BET procedure, using nitrogen adsorption taken in the relative equilibrium pressure interval of 0.03–0.3. Mesopores mean pore size and its distribution were calculated using the BJH method from desorption isotherms. The TiO_2 and zeolite based samples (15–20 mg) were previously degassed under nitrogen flow and under vacuum, respectively, at 350 °C for 4 h.

Catalysts surface acidity was measured by temperature programmed desorption of NH_3 (NH_3 -TPD) performed on a Micromeritics AutoChem 2910 instrument. Prior to adsorption experiments, the samples (15–20 mg) were pretreated in a quartz U-tube under 5% O_2 /He mixture gas flow (50 mL/min) at 500 °C for 45 min, cooled down to 100 °C and treated with helium (50 mL/min) for 60 min. The adsorption step was performed by admitting small pulses of NH_3 in helium (10% NH_3 /He) at 100 °C up to saturation. Subsequently, the samples were exposed to a flow of helium (50 mL/min) for 2 h at 100 °C in order to remove reversibly and physically bound NH_3 from the surface. Finally, TPD was started using helium as carrier gas (50 mL/min) from 100 to 550 °C at a heating rate of 10 °C/min, while the NH_3 desorption was continuously monitored with a TCD detector. The amount of NH_3 desorbed was determined by time integrated NH_3 -TPD curves as a measure of the acid site concentration.

Redox behavior was examined by temperature programmed reduction using H_2 (H_2 -TPR). The experiments were conducted on a Micromeritics AutoChem 2920 instrument. Firstly, all the samples (15–20 mg) were pre-treated under 50 mL/min of 5% O_2 /He mixture at 500 °C for 45 min and then cooled down to room temperature and flushed with helium for 60 min. Then samples were heated

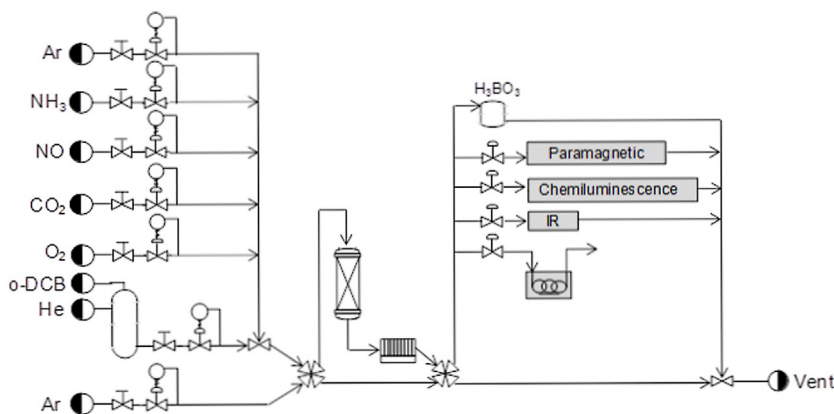


Fig. 1. Experimental set-up.

from room temperature to 1000 °C at a rate of 10 °C/min under a 50 mL/min of 5% H₂/Ar mixture gas flow. The water produced by reduction was removed in a cold trap, and the consumption of H₂ was continuously monitored with a TCD detector. The total amount of H₂ consumption was calculated from time integrated H₂-TPR curves.

X-ray diffraction (XRD) studies were conducted on a Philips PW 1710 X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and Ni filter. The finely grounded samples were scanned between 10° (2 θ) and 70° (2 θ) with 0.02°/s sampling interval. Phase identification was conducted by comparison with JCPDS (Joint Committee on Powder Diffraction Standards) database cards.

2.3. Experimental reaction set-up and catalytic tests

The experimental reaction set-up is shown in Fig. 1. The gas mixture was fixed in order to simulate as best as possible the MWI real feed. Due to the difficulty of handling such toxic PCDD/Fs, researchers usually work with less toxic model molecules and with a chemical structure similar to that of PCDD/Fs such as *o*-DCB [8,11]. Thus, the catalytic reactor feed consisted of O₂ (10%), CO₂ (10%), NO (300 ppm), NH₃ (300 ppm), *o*-DCB (100 ppm) and balanced Ar. The gas flows were regulated by gas mass flow controllers (Bronkhorst® High-Tech F-201CV) whereas *o*-DCB liquid stream was dosed by a Bronkhorst® High-Tech μ -Flow L01-AAA-99-0-20S mass flow controller. The complete evaporation of the liquid stream and homogenous blend with the gas stream was performed in a controlled-evaporator-mixer (Bronkhorst® High-Tech W-102A-111-K). In order to avoid gas adsorption and condensation in the pipes, these were heated with electrical resistances. The resulting gaseous stream went through the fixed catalytic bed inside a U-shaped tubular quartz reactor (13.6 mm), which was heated into a convective-flow oven. Before catalytic measurement, the fixed bed was dried at 200 °C during 2 h in pure argon flow (2 L_N/min). Catalytic tests were performed as light-off curve at 1.5 atm pressure by feeding constant total flow of 2 L_N/min and increasing temperature from 100 to 500 °C with a constant heating rate of 1.5 °C/min. The catalytic bed consisted of 1.5 g of particulate catalysts (0.3–0.5 mm) mixed with inert quartz (0.5–0.8 mm) in order to fill a bed volume of 3 mL, resulting in a GHSV value of 40,000 h⁻¹.

An on-line gas chromatograph (Agilent Technologies 7890A) equipped with a HP-VOC capillary column and a mass selective detector 5975C was used to quantify *o*-DCB concentration in the reactor inlet and outlet streams and also to detect possible reaction hydrocarbon sub-products. Furthermore, NO was continuously measured using chemiluminescence analyzer. CO₂, CO and N₂O were analyzed with infrared, whereas O₂ with paramagnetic detector, all of them integrated in NGA 200 Rosemount Analytical

analyzers. During the reaction it was difficult to follow NH₃ due to its reaction with HCl (product of *o*-DCB oxidation) and the subsequent NH₄Cl formation. For this, NH₃ was only measured before reaction to verify its concentration by titration. The feed, without CO₂, was passed through a solution of boric acid (0.005 M) for some time and then, the amount of NH₃ which reacted with boric acid was determined by measuring the amount of hydrochloric acid solution (0.1 N) required to bring the pH to its initial value. Phenol Red, with a pH range of 6.6 (yellow)–8.0 (red), was used as an indicator.

Since zeolites contain narrow pores, which are size selective, accessibility of reactants have been checked beforehand by means of a diagnostic test for the analysis of intraparticle mass transfer limitation. The test consists of determining the isothermal conversion for particles of different size at constant space velocity (Fig. 2). This was set to 144 L_N/(h g) instead of 80 L_N/(h g), in order to obtain higher reaction rates and thus guarantee a wider range of conditions in absence of internal mass transfer limitation. As shown in Fig. 2 conversion of NO and *o*-DCB did not vary in the whole range of 0.1–0.9 mm particle size, which confirms the absence of mass transfer limitation inside the zeolite narrow pores. Although the relatively large size of PCDD/Fs compared to *o*-DCB, this results could be extrapolated due to the wide range of conditions checked. In addition, external mass transfers limitation are confirmed by Mears criteria (0.015 < 0.15) [22].

A reproducibility test of the catalytic reaction was performed by repeating the same light-off test (control test) regularly as shown elsewhere [6]. NO conversion exhibits a constant standard deviation around 1.5% in the whole range of temperature. However,

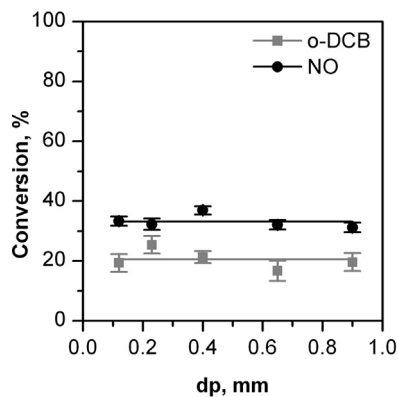
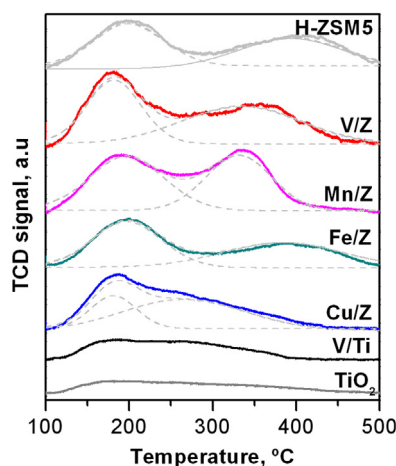
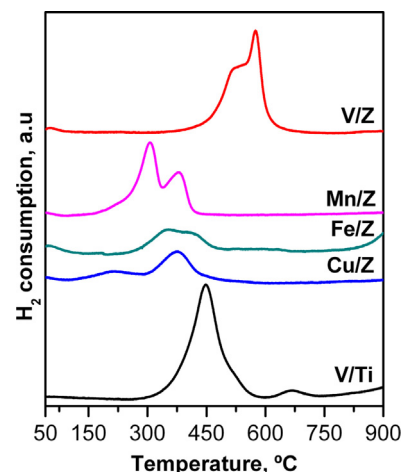


Fig. 2. Conversion of *o*-DCB and NO with different V/Z catalyst particle sizes (100 ppm *o*-DCB, 300 ppm NO, 300 ppm NH₃, 10% O₂, 10% CO₂, 1.2 L_N/min, 1.5 atm and 144 L_N/(h g)).

Fig. 3. NH_3 -TPD profiles.Fig. 4. H_2 -TPR profiles.

standard deviation of *o*-DCB conversion increases up to 5% as the slope of the light-off curve increases, due to the high sensitivity of *o*-DCB oxidation to the temperature.

3. Results and discussion

3.1. Characterization

Chemical composition of prepared catalysts as well as basic characterization results are summarized in Table 1. Metal content of ion exchanged catalysts, Cu/Z and Fe/Z, is slightly lower than impregnated V/Z and Mn/Z catalysts. Isotherms of zeolites (not shown for brevity) fit to type I IUPAC classification, characteristic of microporous materials. However, the reference V/Ti catalyst isotherm is identified as type IV, assignable to mesoporous materials. Therefore, zeolite based catalysts have significantly higher surface area than the reference V/Ti due to their microporosity. The addition of any metal to both supports, H-ZSM5 and TiO_2 , leads to surface area loss. Cu/Z has the highest surface area of $372 \text{ m}^2/\text{g}$ whereas V/T catalyst BET surface area is $59 \text{ m}^2/\text{g}$. In addition, mesopores mean pore size is also bigger in V/T catalyst than in zeolites. The former shows 128 \AA average pore size whereas zeolite samples show c.a. 55 \AA .

Catalysts NH_3 -TPD profiles are shown in Fig. 3 and the quantitative results are summarized in Table 1. As expected the acidity of zeolites ($0.79\text{--}0.45 \text{ mmol NH}_3/\text{g}$) is significantly higher than the reference V/T catalyst ($0.23 \text{ mmol NH}_3/\text{g}$). The addition of a metal on H-ZSM5 by impregnation method leads to an increase of surface acidity while by ion exchange the acidity decreases. Thus, V/Z and Mn/Z samples prepared by impregnation method are more acidic than ion exchanged Cu/Z and Fe/Z catalysts because the later method is more selective to acid protons [23]. The presence of VO_x species over TiO_2 surface also provides acid centers. According to the literature, TiO_2 as anatase crystalline structure only shows Lewis acid sites and the addition of VO_x allows the conversion of the V=O band to the V-OH band, giving a little amount of Brønsted acid sites as a result [9].

NH_3 -TPD profiles of zeolite catalysts show two major NH_3 desorption peaks characteristic of H-ZSM5 support. A desorption peak around $180\text{--}200^\circ\text{C}$ is considered as corresponding to weak acid sites, while the peak c.a. 400°C is considered as corresponding to strong acid sites [24]. However, TiO_2 support and consequently V/Ti sample show a unique broad NH_3 desorption peak from 120 to 400°C [25]. NH_3 -TPD curves were fitted to two Gaussian functions associated with desorption at low and high temperatures, respectively, in such a way that the contribution of weak and strong acid

sites was calculated by time integration of each fitting to a Gaussian curve. The fitting quality of the deconvolution, measured as correlation coefficient (R^2) of least square fitting, was always higher than 0.8. The amount of strong and weak acid sites is shown in Table 1. Cu/Z shows the highest contribution of weak acid sites, since its NH_3 -TPD profile is broad and it shows medium strength acid sites (250°C) high contribution. Otherwise, V/Z shows the highest contribution of strong acid sites.

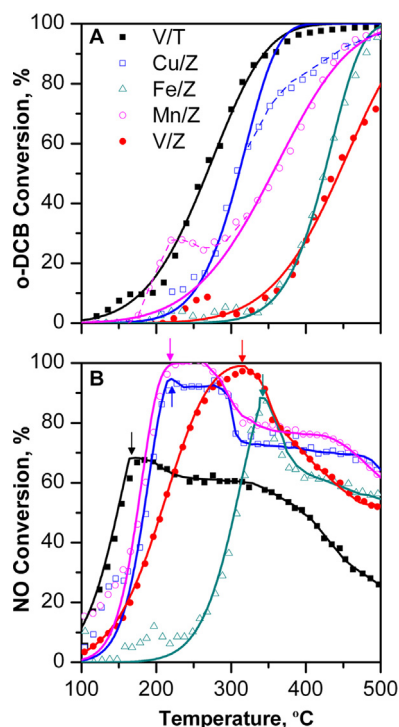
H_2 -TPR profiles of metal exchanged together with V/T sample are shown in Fig. 4. Moreover, Table 1 shows reduction temperatures and quantitative results in terms of consumed H_2 moles per metal mol since this ratio is indicative of different metal species. Cu/Z reduction starts at lowest temperature followed by Mn/Z, Fe/Z, reference V/T and V/Z, respectively. Cu/Z reduction profile shows two reduction peaks indicative of different species. The maximum around 200°C corresponds to the reduction of bulk CuO species and the peak at 375°C could be assigned to the reduction of Cu^{+2} cations exchanged on the zeolite [12]. The quantitative H_2 -TPR results ($\text{H}_2/\text{Cu} = 1.05$) confirmed that all the Cu was as Cu(II) and all species were completely reduced to metal copper (Cu^0). Both species are important in the SCR reaction: bulk CuO catalyzes the oxidation of NO to NO_2 and Cu^{+2} ions maintain high NO_x conversion at high temperature [12,26]. In addition of that, the presence of NO_2 is beneficial for *o*-DCB oxidation because it has higher oxidative potential than O_2 [13,14].

Mn/Z catalyst also shows two reduction peaks. The first reduction peak (305°C) is associated with highly dispersed and easily reducible MnO_2 whereas the second reduction peak (380°C) is associated to the reduction of Mn_2O_3 directly to MnO or bulk MnO_x phase [20,27]. Quantitative results confirm that both species, MnO_2 and Mn_2O_3 , coexisted on the surface of supported Mn/Z catalyst. The nominal ratios of H_2 consumed per Mn atom (H_2/Mn) to reduce completely MnO_2 and Mn_2O_3 to MnO are 1 and 0.5, respectively. Mn/Z shows the H_2/Mn ratio of 0.59. According to the literature, MnO_2 seems to be the most active species in both reactions [20,21].

H_2 -TPR profile of Fe/ZSM5 shows three zones of H_2 consumption: $240\text{--}480$, $480\text{--}680$ and $>800^\circ\text{C}$. In the first range two small peaks are distinguishing which could correspond to the reduction of Fe_2O_3 into Fe_3O_4 and/or FeO (350°C) and to the reduction of Fe_3O_4 small nanoclusters to FeO (415°C) [17]. A broad reduction peak between 753 and 953°C could be associated to the reduction of Fe^{+2} ions to Fe^0 and finally the peak above 800°C is due to slow reduction of Fe^{+2} attached to zeolite framework to Fe^0 [26,28]. Overall reduction of Fe_2O_3 consumes a H_2/Fe ratio of 1.5 and the experimental 0.85 data indicates that all Fe^{+3} was not reduced com-

Table 1
Characterization results.

Sample	Chemical composition	Textural properties			Redox properties		Acid property		
	CM, %wt.	S_{BET} m ² /g ⁻¹	V_p cm ³ g ⁻¹	D_p Å	Reduction temperature °C	H ₂ /M	NH ₃ consumption, mmol NH ₃ g ⁻¹	Weak (%)	Strong (%)
V/Ti	2.94	59	0.24	128	450	1.01	0.23	—	—
Cu/Z	1.60	372	0.14	49.4	214	1.05	0.52	0.56	0.44
Fe/Z	2.04	283	0.18	61.5	353	0.85	0.45	0.53	0.47
Mn/Z	3.67	294	0.14	56.0	305	0.59	0.75	0.52	0.48
V/Z	3.42	361	0.19	56.6	522	0.74	0.79	0.45	0.55
TiO ₂	—	70	0.31	146	—	—	0.17	—	—
H-ZSM5	—	390	0.11	44.4	—	—	0.60	0.49	0.51

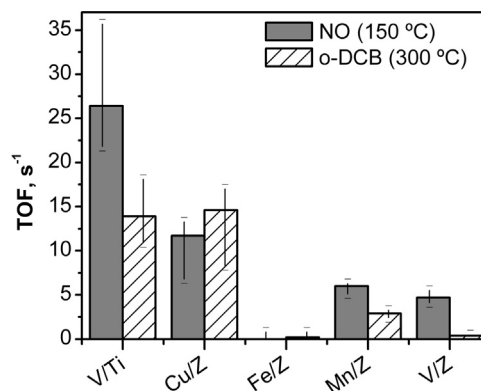
**Fig. 5.** Ignition curves of (A) *o*-DCB oxidation and (B) NO reduction in a simulated MSW off-gas (100 ppm *o*-DCB, 300 ppm NO, 300 ppm NH₃, 10% O₂, 10% CO₂, 2 L_N min⁻¹, 1.5 atm and 80 L_N (h g)⁻¹).

pletely to Fe⁰ as it is clearly observed with an unfinished reduction peak at high temperature [29].

Finally, V/Z catalysts show two reduction peaks at 515 °C and 575 °C whereas V/Ti catalyst shows a unique H₂ consumption peak at lower temperature (450 °C) evidencing the higher reducibility of the latter. It is well established in the literature that monomeric VO_x species are the most reducible species, followed by polymeric, amorphous and crystalline V₂O₅ species, respectively [6,30]. This result suggests that V/Ti sample is composed by highly dispersed monolayer VO_x species, either isolated VO₄ or polymeric (VO₄)_n. Otherwise, two reduction peaks on V/Z catalyst is indicative of crystalline V₂O₅ reduction [30]. In a previous work it was concluded that monomeric species are the most active for *o*-DCB oxidation whereas polymeric for NO reduction [6].

3.1.1. Catalytic performance

Catalytic activity of metal/zeolites in the combined removal of NO and *o*-DCB was characterized by monitoring the conversion as a function of temperature under above shown conditions. Fig. 5 shows the characteristic curve, referred as ignition or light-off curve obtained for the conversion of *o*-DCB and NO, respectively. NO reduction takes place at lower temperature than *o*-DCB oxidation over all the catalysts [5]. *o*-DCB conversion shows the typical

**Fig. 6.** TOF values of *o*-DCB oxidation (300 °C) and NO reduction (150 °C).

S-shaped light-off for the hydrocarbon oxidation, but NO conversion follows the same shape just up to a maximum conversion, which is located at a different temperature for each catalyst. Subsequently, NO conversion decreases, due to the competition between NO reduction and NH₃ oxidation as the temperature increases, as we already detailed elsewhere [6]. Since the metal content is not exactly the same in all the samples, the turn over frequency (TOF) were calculated assuming the first order reactions (Eq. (3)) at 150 °C and 300 °C in case of NO reduction (the temperature at which the SCR reaction shows high selectivity) and *o*-DCB oxidation reaction, respectively (Fig. 6). Both reactions are well described by the first order kinetic noted by the low deviation of the ignition curves (Fig. 5) experimental data shown as symbols from the line obtained for first order kinetic equation. *o*-DCB oxidation reaction ignition curves fit properly in the whole temperature range. However, NO conversion is well fitted up to the maximum conversion indicated with an arrow since above corresponding temperature competing NH₃ oxidation overcome SCR reaction,

$$\text{TOF} = \frac{F_0 \times \ln(1 - X_A)/(W \times X_V/\text{MW}_V)}{P_T} \quad (3)$$

where F_0 is the reactive initial molar flow, X_V is the catalyst vanadium mass fraction, MW_V is vanadium molecular weight and P_T is the reactor pressure.

The reference V/T catalyst shows the best catalytic performance at low temperature, since the highest *o*-DCB and NO conversions are achieved (Fig. 5). Cu/Z and Mn/Z ignition curves are slightly shifted to higher temperature whereas V/Z and Fe/Z show significantly lower catalytic performance, especially for *o*-DCB oxidation reaction. Thus, the activity order for *o*-DCB oxidation regarding T_{50} (temperature for 50% conversion, °C) value is: V/T (265) > Cu/Z (310) > Mn/Z (365) > Fe/Z (420) > V/Z (430), whereas the activity order for NO reduction is V/T (150) > Mn/Z (178) > Cu/Z (185) > V/Z (205) > Fe/Z (310).

However, the lowest metal content of ion exchanged Cu/Z catalyst make it the catalyst with highest specific catalytic activity in *o*-DCB oxidation ($\text{TOF} = 15.7 \times 10^{-5} \text{ s}^{-1}$) closely followed by the

reference V/T sample ($\text{TOF} = 14.5 \times 10^{-5} \text{ s}^{-1}$), as shown in Fig. 6. Similarly, though the ignition curves of Cu/Z and Mn/Z for NO reduction are very close, the former shows significantly higher TOF value. Mn/Z ($6.07 \times 10^{-5} \text{ s}^{-1}$) and V/Z ($4.65 \times 10^{-5} \text{ s}^{-1}$) show similar TOF value for NO reduction whereas Mn/Z ($3.1 \times 10^{-5} \text{ s}^{-1}$) is considerably more active than V/Z ($0.4 \times 10^{-5} \text{ s}^{-1}$) on *o*-DCB oxidation. Finally, Fe/Z is by far the less active catalyst for both reactions. Noteworthy that Cu/Z also show the lower reduction temperature (Table 1) followed by Mn/Z, Fe/Z, V/T and V/Z respectively.

Not only reducibility, but also the higher acidity of metal/zeolites plays an important role. The outstanding feature of metal/zeolites is the maximum conversion of NO reached and kept high in a broader temperature range before NH_3 oxidation prevail over NO reduction. At most, 68% of NO conversion is obtained at 180°C with V/Ti catalyst, whereas almost 100% is obtained with all the zeolitic based catalysts. Higher NO conversion is recorded using M/Z and V/Z samples ($\sim 100\%$) than with Cu/Z and Fe/Z. This feature is closely related with acidity as shown in Table 1 [24]. Most acid catalysts are M/Z and V/Z followed by Cu/Z and Fe/Z. This characteristic provides some advantages to metal/zeolites: on the one hand they are less selective to undesired NH_3 oxidation reaction, which requires higher temperatures to overtake the NO SCR reaction; on the other hand the working window (temperature range where NO conversion is maintained high) is wider, in such a way that metal/zeolites are more likely to produce high conversion of both pollutants, NO and *o*-DCB, simultaneously in wider temperature range.

Assuming that the working window is defined as the temperature range at which conversion of 60% or higher is reached for both pollutants. Cu/Z is the catalyst with the wider working window, as shown in Table 2. Although reference V/T catalyst working window is obtained at lower temperature than zeolitic catalysts, which means lower reheating costs of the flue gas, the working window amplitude is quite limited (40°C). Most active Cu/Z and Mn/Z catalysts working window amplitudes are 200 and 130°C , respectively. The lower activity of V/Z and Fe/Z in the oxidation of *o*-DCB, leads to a very narrow window or even to the absence.

Higher acidity of metal/zeolites also influences on the *o*-DCB conversion. The light-off curves of *o*-DCB oxidation over the most acidic metal/zeolites (Mn/Z and V/Z) show a noticeable positive deviation from the typical S-shape in the low conversion region, resulting in a small peak of conversion. Deviation over the samples with intermediate level of acidity (Cu/Z and Fe/Z) is notably lower, while over V/T (low acidity) such deviation is almost indiscernible. This phenomenon looks to be linked to the first stage of adsorption of *o*-DCB on acidic centers through the chlorine atom(s) [8,9]. In this sense Mn/Z catalysts deviation for the light-off curve is significantly more severe than the rest of the catalysts (noted by dotted line). Yan et al. [27] and Wang et al. [31] attributed this feature to the MnO_x poisoning due to chlorine adsorption at low temperature.

Apparent activation energy was calculated using the fitted light-off curves (Table 2). As it is mentioned previously, Mn/Z catalyst self-poisoning due to chlorine adsorption is observed at low temperature (160 – 250°C) [27,31]. Therefore, data between 100 and 160°C were used to calculate NO reduction activation energy, where data above 300°C in case of *o*-DCB oxidation reaction. Vanadia based (V/T and V/Z) catalysts' activation energy is significantly lower than Cu/Z, Fe/Z and Mn/Z in NO reduction. Similar values of NO_x reduction reaction activation energies are reported in the literature [15,32]. In case of *o*-DCB oxidation, more differences between estimated activation energies are obtained. V/T is also the sample with the lowest activation energy followed by Mn/Z, V/Z, Cu/Z and Fe/Z, respectively.

Reaction selectivity is also an important aspect for catalysts used for pollutant abatement, since toxic by-products are not desired.

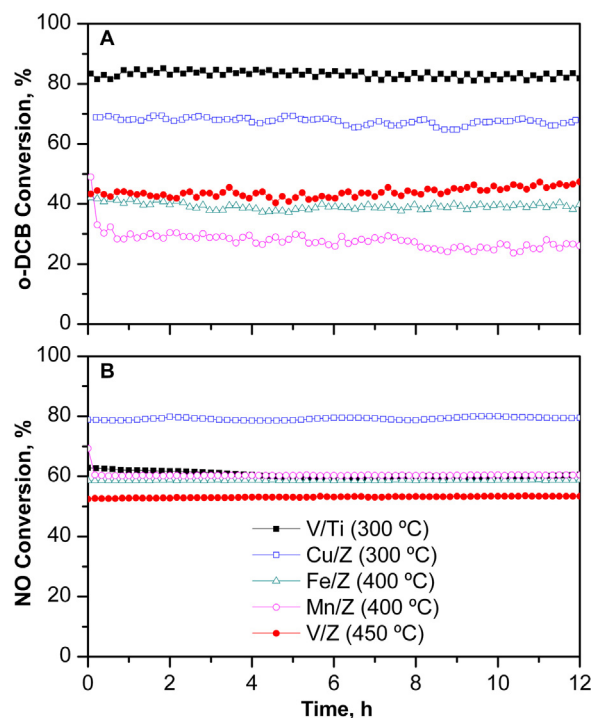


Fig. 7. Stability tests of (A) *o*-DCB oxidation and (B) NO reduction in a simulated MSW off-gas (100 ppm *o*-DCB, 300 ppm NO, 300 ppm NH_3 , 10% O_2 , 10% CO_2 , $2\text{L}_\text{N} \text{ min}^{-1}$, 1.5 atm and $80 \text{ L}_\text{N} (\text{h g})^{-1}$).

Table 2 shows obtained CO, N_2O and poly-chlorinated hydrocarbons maximum concentrations. Zeolite based catalysts form less CO than the reference V/T catalyst. Nevertheless, metal/zeolites produce also trichlorobenzene (TCB) evidencing the presence of chlorinated reaction. In this sense, zeolites are reported to be very active in the catalytic liquid phase chlorination of *o*-DCB to 1,2,4-TCB [33]. Although TCB was detected as trace (0.5 – 4 ppm) over Mn/Z, V/Z and Fe/Z, TCB is formed in significant quantities (30 ppm) over Cu/Z since CuO is highly efficient catalyzing PCDD/Fs formation from chlorinated aromatic compounds [34]. TCB formation starts around 300°C and show a maximum of its formation c.a 370°C . Since the formation of 1 mol of TCB requires 1.5 mols of *o*-DCB, 45% of selectivity to TCB is estimated. Moreover, with Cu/Z traces of tetrachloroethylene were also detected. Therefore, it can be concluded that Cu/Z catalyst' high catalytic activity on *o*-DCB oxidation reaction is due to the sum of chlorination and oxidation reactions. This explains the lower fitting of ignition curve to first-order kinetic in the oxidation of *o*-DCB at high temperature over Cu/Z catalyst (Fig. 5).

On the other hand, N_2O is practically negligible with all the zeolite based catalysts, evidencing low selectivity for NH_3 oxidation reaction as we previously concluded. Maximum 20 ppm of N_2O are obtained with all of them except with Mn/Z, with which 40 ppm are formed at 270°C , temperature where maximum NO conversion is obtained. Therefore, higher selectivity to N_2 and lower selectivity to NH_3 oxidation reactions are expected with zeolite based catalysts than with the reference V/T.

Catalysts' stability is an important factor for commercial scale applicability. Then, samples durability was measured during 12 h reaction tests at a constant temperature. Temperatures were chosen near the working window. As shown in Fig. 7 all the catalysts are stable in the studied reaction conditions. Only, *o*-DCB and NO conversions decay a bit in the begging of the reaction over Mn/Z catalyst, that could be due to chlorine adsorption [27,31], though this sentences deserves further research.

Table 2
Activity measurements results.

Sample	Working window, °C	Ea, KJ/mol		Maximum concentration, ppm		
		NO	<i>o</i> -DCB	CO	TCB ^a	N ₂ O
V/Ti	285–330 (40)	47 ± 0.70	43 ± 2.30	320	0	120
Cu/Z	320–520 (200)	81 ± 1.41	77 ± 2.94	125	30	15
Fe/Z	430–440 (10)	89 ± 1.25	113 ± 2.25	180	3	0
Mn/Z	370–500 (130)	82 ± 1.39	46 ± 1.44	125	4	40
V/Z	—	43 ± 0.24	69 ± 2.21	100	0.5	20

^a Arbitrary concentration estimated by standard liquids patterns.

Table 3
Air emission limit values in the Annex V of Directive 2000/76/EC [1] and the calculated F_{\min} factor for each catalyst.

Pollutant	Daily averages limits in 2000/76/EC (L)	Sample	F_{\min}	T_{opt} , °C	$X_{\text{A,NO}}$ (%)	$X_{\text{A,o-DCB}}$ (%)
NO _x	200 mg/m ³	Cu/Z	29.6	500	64.6	96.0
PCDD/Fs	0.1 ngTEQ/m ³	Fe/Z	12.3	500	57.6	98.6
N ₂ O	n/a	Mn/Z	9.7	500	61.7	97.4
CO	50 mg/m ³	V/Z	23.2	500	38.0	90.5

The data shown so far confirm that zeolite catalysts are able to abate concurrently NO and *o*-DCB from MWI off-gases. The choice of the best catalyst it is not an easy task, since each sample shows advantages and disadvantages, as shown above. For instance, Cu/Z is the most active metal/zeolite with the widest working window and the highest *o*-DCB oxidation capability but unfortunately, high amount of TCB is formed. Mn/Z and V/Z are more active in NO reduction but less active in *o*-DCB oxidation. Otherwise, Fe/Z is the less active catalyst but is also less selective to N₂O. Since their performance has been analyzed for an environmental application, a selection based upon both environmental and energetic criteria can be made. A numerical F factor has been calculated, including the limit values for incineration plant emissions to air as set out in Annex V to the Directive 2000/76/EC [1]. They concern PCDD/Fs, CO, NO and NO₂, and N₂O. The F factor is defined as the sum of the reactor outlet pollutants concentration multiplied by a factor of penalty defined as the inverse of the emission limit, both in ppm (4). Therefore, the more suitable catalyst should be the one that show the lowest F value at the lowest operating temperature. Table 3 shows the emission limits according to Directive 2000/76/EC and the minimum value of the F factor (F_{\min}) with the corresponding temperature (T_{opt}); conversion of NO and *o*-DCB are also shown.

$$F = C_{\text{o-DCB}} \times \frac{1}{L_{\text{PCDD/Fs}}} + C_{\text{NO}} \times \frac{1}{L_{\text{NO}}} + C_{\text{CO}} \times \frac{1}{L_{\text{CO}}} + C_{\text{TCB}} \times \frac{1}{L_{\text{PCDD/Fs}}} \quad (4)$$

It is noteworthy that the in this work 100 ppm of *o*-DCB was fed as representative of the PCDD/Fs, as noted above, although in MWI plants PCDD/Fs are found in significantly lower concentration. Then, the calculation of F was done by assuming that the catalytic reactor inlet of PCDD/Fs is 21 ngTEQ/Nm³ [35]. TCB was also supposed to be a PCDD/F, then outlet concentration of PCDD/Fs was calculated based on *o*-DCB conversion and TCB selectivity.

According to Table 3, PCDD/Fs emission limit is by far the lowest value, so the resulting F value is strongly limited by it. Then Mn/Z should be the most suitable catalyst, followed by Fe/Z, both accounting the highest *o*-DCB conversion and the lowest TCB selectivity. Conversely, Cu/Z is the worst catalyst due to the high selectivity to TCB. In all the cases, F value has been minimized at 500 °C.

4. Conclusions

MWI plants have begun to implement a SCR technology using vanadia based -V₂O₅-WO₃ (MoO₃)-TiO₂ catalyst in order to reduce the NO_x. This catalyst also shows good performance in the simultaneous NO-SCR and PCDD/Fs catalytic total oxidation. However TiO₂ low resistance, vanadium high toxicity and low selectivity to N₂ at the temperatures for high conversion of PCDD/Fs due to NH₃ oxidation leads to need for alternative catalyst. Therefore, in this research work the behavior of different metal/ZSM5 catalysts, such as Cu/Z, Fe/Z, Mn/Z and V/Z, is analyzed with the aim to improve simultaneously selectivity to N₂ and conversion of NO in a wider temperature range. Catalysts textural, acid and redox properties have been characterized by N₂ adsorption-desorption isotherms, XRD, NH₃-TPD and H₂-TPR and in general terms zeolites higher surface area, acidity and reducibility have been confirmed.

By catalytic tests carried out in the experimental conditions close to those employed in MWI plants, it was found that Cu/Z is the most active catalyst for both reactions. In case of *o*-DCB oxidation, it shows even higher TOF value than the reference V/T catalyst. Due to its high acidity the selective to NH₃ oxidation reaction is lower (negligible N₂O formation) and therefore higher NO conversion is obtained in a wider operating temperature window. However, its high activity in *o*-DCB oxidation reaction, especially at high temperature is related to its high selectivity to TCB. Mn/Z and V/Z show middle catalytic activity, but only Mn/Z catalysts is deactivated at low temperature, due to chlorine adsorption. Fe/Z is the less active catalyst for both NO reduction and *o*-DCB oxidation reactions could be due to its low reducibility. Both reactions ignition curves are well fit to first order reaction kinetic over all the catalyst.

Mn/Z followed by Fe/Z, operating at 500 °C have been identified as the best choices, based upon both environmental and energetic criteria, due to their higher capability for *o*-DCB oxidation and lower selectivity to TCB. Conversely, Cu/Z is the worst catalyst due to the high selectivity to TCB.

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References

- [1] Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste.
- [2] E. Finocchio, G. Busca, M. Notaro, *Appl. Catal. B* 62 (2006) 12–20.
- [3] R. Weber, T. Sakurai, H. Hagenmaier, *Appl. Catal. B* 20 (1999) 249–256.
- [4] M. Goemans, P. Clarysse, J. Joannès, P. De Clercq, S. Lenaerts, K. Matthys, K. Boels, *Chemosphere* 50 (2003) 489–497.
- [5] J. Jones, J.R.H. Ross, *Catal. Today* 35 (1997) 97–105.
- [6] M. Gallastegi-Villa, A. Aranzabal, Z. Boukha, J.A. González-Marcos, J.R. González-Velasco, M.V. Martínez-Huerta, M.A. Bañares, *Catal. Today* 254 (2015) 2–11.
- [7] N. Topsøe, *Science* 265 (1994) 1217–1219.
- [8] M.A. Larrubia, G. Busca, *Appl. Catal. B* 39 (2002) 343–352.
- [9] S. Albonetti, S. Blasioli, R. Bonelli, J.E. Mengou, S. Scirè, F. Trifirò, *Appl. Catal. A* 341 (2008) 18–25.
- [10] J. Li, H. Chang, L. Ma, J. Hao, R.T. Yang, *Catal. Today* 175 (2011) 147–156.
- [11] F. Bertinchamps, C. Grégoire, E.M. Gaigneaux, *Appl. Catal. B* 66 (2006) 1–9.
- [12] B. Pereda-Ayo, U. De La Torre, M.J. Illán-Gómez, A. Bueno-López, J.R. González-Velasco, *Appl. Catal. B* 147 (2014) 420–428.
- [13] F. Bertinchamps, M. Treinen, N. Blangenois, E.M. Mariage, E.M. Gaigneaux, *J. Catal.* 230 (2005) 493–498.
- [14] Z. Xu, S. Deng, Y. Yang, T. Zhang, Q. Cao, J. Huang, G. Yu, *Chemosphere* 87 (2012) 1032–1038.
- [15] S. Brandenberger, O. Kröcher, A. Tissler, R. Althoff, *Appl. Catal. B* 95 (2010) 348–357.
- [16] P. Boroń, L. Chmielarz, J. Gurgul, K. Łatka, B. Gil, J. Krafft, S. Dzwigaj, *Catal. Today* 235 (2014) 210–225.
- [17] J.A.Z. Pieterse, S. Booneveld, R.W. van den Brink, *Appl. Catal. B* 51 (2004) 215–228.
- [18] R. Gonzalez-Olmos, F.D. Kopinke, K. Mackenzie, A. Georgi, *Environ. Sci. Technol.* 5 (2013) 2353–2360.
- [19] D. Divakar, M. Romero-Sáez, B. Pereda-Ayo, A. Aranzabal, J.A. González-Marcos, J.R. González-Velasco, *Catal. Today* 176 (2011) 357–360.
- [20] D.A. Peña, B.S. Uphade, P.G. Smirniotis, *J. Catal.* 221 (2004) 421–431.
- [21] F.S. Saleh, M.M. Rahman, J. Hazard. Mater. 162 (2009) 1574–1577.
- [22] D.E. Mears, *Ind. Eng. Chem. Process Des. Dev.* 10 (1971) 54–547.
- [23] U. De La Torre, B. Pereda-Ayo, J.R. González-Velasco, *Chem. Eng. J.* 207–208 (2012) 10–17.
- [24] S.S.R. Putluru, A. Riisager, R. Fehrmann, *Appl. Catal. B* 97 (2010) 333–339.
- [25] A.P. Kulkarni, D.S. Muggli, *Appl. Catal. B* 302 (2006) 274–282.
- [26] A. Sultana, M. Sasaki, K. Suzuki, H. Hamada, *Catal. Commun.* 41 (2013) 21–25.
- [27] Y. Liu, M. Luo, Z. Wei, Q. Xin, P. Ying, C. Li, *Appl. Catal. B* 29 (2001) 61–67.
- [28] K. Krishna, M. Makkee, *Catal. Today* 114 (2006) 23–30.
- [29] I. Melián-Cabrera, S. Espinosa, J.C. Groen, B. v/d Linden, F. Kapteijn, J.A. Moulijn, *J. Catal.* 238 (2006) 250–259.
- [30] S. Besselmann, C. Freitag, O. Hinrichsen, M. Muhler, *Phys. Chem. Chem. Phys.* 3 (2001) 4633–4638.
- [31] W. Xingyi, K. Qian, L. Dao, *Appl. Catal. B* 86 (2009) 166–175.
- [32] J. Ochońska-Kryca, M. Iwaniszyń, M. Piątek, P.J. Jodłowski, J. Thomas, A. Kołodziej, J. Łojewska, *Catal. Today* 216 (2013) 135–141.
- [33] S. Sharma, S.G. Hegde, A.P. Singh, *Appl. Catal. A* 162 (1997) 201–211.
- [34] S. Nganai, S.M. Lomnicki, B. Dellinger, *Environ. Sci. Technol.* 45 (2011) 1034–1040.
- [35] H.C. Wang, J.F. Hwang, K.H. Chi, M.B. Chang, *Chemosphere* 67 (2007) 177–184.